

Improved thermoelectric performance in GeTe via pentavalent ion substituentsJ.Rajeev Gandhi^{a,d}, Raman Sankar^{a,b}, Kuei-Hsien Chen^{b,c}, Li-Chyong Chen^c^aInstitute of Physics, Academia Sinica, Nankang, Taipei R.O.C. Taiwan 11529.^bInstitute of Atomic and Molecular sciences, Academia Sinica, Taipei 106, Taiwan^cCenter for Condensed Matter Sciences, National Taiwan University, Taipei 106, Taiwan. Department of^dPhysics, Saveetha School of Engineering, Saveetha University, Chennai-600077, India.

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ABSTRACT

Germanium telluride (GeTe), a semiconductor material, is a complex solid state system with interesting fundamental properties and it serves as a base for high-efficiency thermoelectric materials. Generally, thermoelectric conversion efficiency can be enhanced with appropriate strategies such as doping, alloying, and nanostructuring in the thermoelectric materials. Since there is a significant discrepancy between the electronic and thermal transport data for GeTe-based materials reported in the literature obscuring the baseline knowledge and preventing a clear understanding of the effect of alloying GeTe with various elements, we introduce pentavalent ions into GeTe to enhance the Seebeck coefficient and reduction of thermal conductivity to overcome the discrepancy between the electronic and thermal transport data. A complete study including XRD, Seebeck coefficient, electrical resistivity, and thermal conductivity on Ge rich $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) samples was conducted. All compounds were prepared by solid state reaction and hot press method. From the results, As doping enhances the Seebeck coefficient in the temperature range of 323 to 623 K. Our data show that at 723 K, $\text{Ge}_{0.9}\text{As}_{0.1}\text{Te}$ has a higher power factor about $30 \mu\text{Wcm}^{-1}\text{K}^{-2}$ and much higher than that of pure GeTe about $27 \mu\text{Wcm}^{-1}\text{K}^{-2}$. In addition the significant reduction of thermal conductivity was obtained due to collectively phonon scattering by presence of secondary phases and defects in $\text{Ge}_{1-x}\text{As}_x\text{Te}$. The maximum figure of merit ZT value of ~ 0.7 was obtained for the sample of $\text{Ge}_{0.9}\text{As}_{0.1}\text{Te}$ at 673 K, which is 10% higher than that of pure GeTe.

Key words: Germanium Telluride, solid state synthesis, transport properties, figure of merit**1. INTRODUCTION**

In view of the increase in worldwide energy needs and environmental effects it is important to look for alternative renewable energy sources. The thermoelectric (TE) technology is being seen as the perfect solution for both issues due to its ability to efficiently convert waste heat into electric power without CO_2 emission and to develop cost-effective, pollution-free forms of energy conversion¹⁻³. For ideal thermoelectric materials, figure of merit ZT should be ≥ 1 to obtain a conversion efficiency of $>10\%$. The figure of merit which is used to denote the efficiency of thermoelectric material is expressed by $ZT = S^2\sigma T / k$ where σ - is the electrical conductivity, S-is the Seebeck coefficient, k-is the thermal conductivity of the material and T is the absolute temperature. Since S, σ and k are interdependent for any material it is difficult to search new thermoelectric materials having high efficiency. In order to attain high ZT values, high Seebeck coefficient, low electrical resistivity and low thermal conductivity must be achieved. So many strategies, such as the creation of interfaces with

control of crystallographic texture, the reduction of grain size to nanocrystalline dimensions, and the formation of nanocomposite structures, affect each of these properties. The traditional thermoelectric alloys as major material systems have reached much higher thermoelectric performances by band engineering, nano structuring, and so on^{4,5}. P-type PbTe and SnTe have long been studied as TE materials, but GeTe, another member of the group IV monote tellurides, has been less studied. PbTe and SnTe both have a higher-energy L and a lower-energy Σ valence band. In pristine materials with optimized carrier concentrations, the lower-energy offset between these two bands in PbTe compared with that in SnTe leads to a much higher-power factor ($30 \mu\text{Wcm}^{-1}\text{K}^{-2}$)⁶ for PbTe than that for SnTe ($20 \mu\text{Wcm}^{-1}\text{K}^{-2}$)⁷. For GeTe, the available literature shows high a power factor, which is the highest among the three compounds. The underlying origin of this phenomenon, however, is ambiguous, to our best knowledge. The lack of a detailed investigation of GeTe has also hindered the understanding of some GeTe-based alloys with decent TE properties, such as GeTe-AgSbTe (TAGS), $(\text{GeTe})_n\text{Sb}_2\text{Te}_3$ (GST),

$(\text{Bi}_2\text{Te}_3)_x(\text{GeTe})_{1-x}$ and $\text{Ge}_{1-x}\text{Pb}_x\text{Te}$. Therefore, it is of great importance to reveal the essence of the superior electronic performance in GeTe, particularly from the perspective of the electronic structure⁶. GeTe undergoes the ferroelectric structural phase transition from high temperature cubic (β -phase) to low temperature rhombohedral (α -phase) at ~ 700 K due to the thermal strain-induced shift in Ge atoms (Figure 1a), which thrusts the distortion in the unit cell along [111] direction with an angular distortion of $\alpha = 1.65^\circ$ ⁸. In present work we report an effective way of enhancing the thermoelectric properties of GeTe by using a doping element (As) of the same group on Sb doped GeTe. In order to understand the system, we have systematically studied the thermoelectric properties of GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) samples was conducted.

2. EXPERIMENTAL PROCEDURE

2.1 SAMPLE PREPARATION

Samples were prepared by direct reaction of high purity constituent elements in stoichiometric quantity weighed from Germanium (Aldrich 99.999%), Arsenic (Aldrich 99.999%) and Tellurium (Aldrich 99.997%) without further purification. High quality poly crystalline ingots (~ 6 g) of GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) were synthesized by solid state reaction and hot press method. The concern elements in composition were collected in quartz ampoules and evacuated to high vacuum of $\sim 10^{-5}$ Torr, then heated up to 873 K (rate of 2K min^{-1}) for 12 hours and gradually cooled to room temperature. The collected samples were annealed further up to 863 K for 24 hrs. The obtained ingot was powdered by agate mortar; structural and phase confirmation of the samples were verified by room temperature x-ray diffraction using a Rigaku X-ray diffractometer with a $\text{Cu-K}\alpha$ X-ray radiation ($\lambda = 1.5406\text{\AA}$). The powders were consolidated into a bulk pellet by graphite die (~ 20 mm) using hot press method at 773 K with pressure of $P = 45$ Mpa for 30 min for analyzing Thermoelectric properties. The prepared pellets were cut in to different dimensions by diamond wheel saw and polished. The cut and polished samples were studied for thermoelectric transport property and thermal diffusivity.

2.2. CHARACTERIZATION

All the powder samples phase purity and structural analysis were carried out by using the Powder X-Ray Diffraction (PXRD) of Bruker D8 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{\AA}$). In order to understand the temperature dependent structural analysis (Phase change analysis) of the prepared samples synchrotron X-ray diffraction (XRD) at different temperatures was studied in

Taiwan photon source (TPS) with 0.9\AA beam line situated at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Charge transport properties such as electrical conductivity (σ) and Seebeck coefficient (S) measurements from 300 - 773 K were performed on a parallelepiped shaped ($3 \times 2 \times 15\text{ mm}^3$) cut and polished pellet under Helium gas atmosphere by ULVAC-RIKO ZEM-3 instrument. The longer direction coincides with the direction in which the thermal conductivity was measured. The thermal diffusivity (D) measurements were performed from 300 - 773 K on a as sintered pellets of 6 mm diameter and thickness of ~ 2 mm using laser flash system (Netzsch, LFA -457); also the temperature dependent specific heat capacity (C_p) at constant pressure was derived using a standard sample (pyroceram) by LFA-457, which is in good agreement with Dulong-Petit C_p value. The total thermal conductivity (κ) was calculated using the formula $\kappa = DC_p\rho$, where ρ is the density. Using the conventional Archimedes method, the density of pellets was measured to be $\sim 99\%$ of its theoretical density.

3. RESULTS AND DISCUSSIONS

Figure 1 represents the XRD patterns of the synthesized powders with composition of GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15). The incorporation of As in GeTe constructs the secondary As-rich. PXRD patterns of the samples confirm that GeTe having the single phase, whereas As doped samples are having mixed phases it is clearly indicated in Figure 1 by diamond shapes. All the XRD patterns are resemble rhombohedral ($R3m$)⁹ phases of GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) by solid state reaction and hot-press technique.

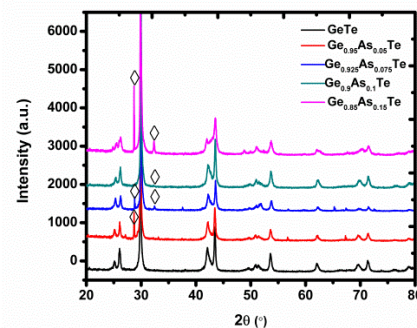


Fig. 1 PXRD patterns of GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) samples. The As-rich secondary phase is indicated by the diamond shapes.

So many reports revealed the temperature dependence phase transformation in GeTe; in order to understand such transformation we have

performed the synchrotron X-Ray Diffraction at different temperatures for $\text{Ge}_{0.9}\text{As}_{0.1}\text{Te}$ sample which have higher ZT is shown in Figure 2. The phase transformation clearly shown at 623K; at this transformation the crystal rearrangement makes it high electric conductive than the previous phase due to symmetric cubic structure formation and it may be due to the thermal strain-induced shift in Ge atoms, which thrusts the distortion in the unit cell along [111] direction with an angular change of $\alpha=1.65^\circ$. Subsequently the when this sample were cooled down to 303 K the structure of sample were changed to rhombohedral R3m phase. One more fascinating feature was clearly observed that the peak doublets ($2\theta \sim 41 - 45^\circ$) were forming a double peak¹⁰ indicating the rhombohedral R3m structure at RT¹⁰.

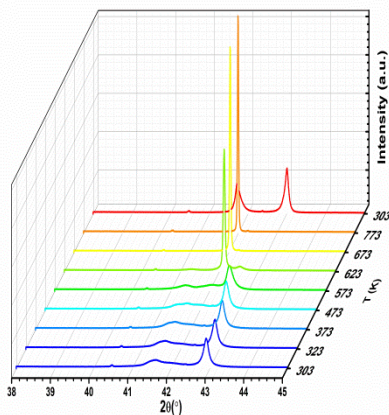


Fig. 2 Temperature dependent synchrotron X-ray diffraction (XRD) data for $\text{Ge}_{0.9}\text{As}_{0.1}\text{Te}$ sample.

GeTe undergoes a phase transition from the rhombohedral to a rock salt structure at 673 K¹¹. Similarly $\text{Ge}_{0.9-x}\text{As}_x\text{Te}$ undergoes ordering transitions at high temperature (~ 623 K) rhombohedral to rock salt phase. This phase transition has been described as a semiconductor to metal transition due to Anderson localization.¹² The phase transition starts from 623 K by ordering of As and Ge and vacancies on the cation sites. The resulting structure of rhombohedral can be described as alternating layers of Ge, As, and Te with interpenetrating vacancy layers; which tend to lower the thermal conductivity in these compounds.¹³ The phase transition is accompanied by a significant decrease in the electrical resistivity, while the Seebeck coefficient and thermal conductivity are relatively unaltered ensuing in higher ZT.¹⁴

Temperature dependent transport properties of the As doped samples of GeTe was symbolized in

Figure 3-5. Figure 3 corresponds to temperature dependence electrical conductivity of the GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) samples. The σ of doped sample decreases with increasing the temperature indicating degenerate semiconductor behavior. Substitution of As in GeTe drastically decreases the σ indeed suppresses the Ge vacancies and decreases the carrier concentration. The effect of phase transformation was clearly visible in σ of As doped GeTe ; a significant increment in σ was observed while phase transformation and it helps to enhance in the power factor value.

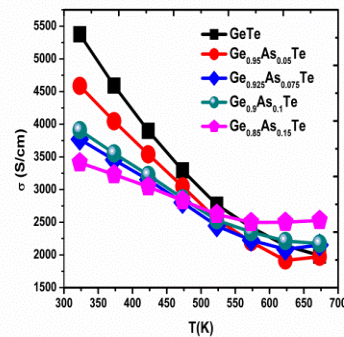


Fig. 3. The temperature dependent electrical conductivity of GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) samples.

Figure 4 represents the temperature dependent Seebeck coefficient and all the samples follow the converse trend of σ . All doped samples have shown highest S values of $\sim 125 \mu\text{V/K}$ at 673 K. We have cross checked our results by multiple hot and cool cycles from 300 – 673 K; it was found that the properties were reproducible and stable across all cycles of heating and cooling with a hysteresis about the phase transition.¹⁵ The electrical resistivity and Seebeck coefficient increases for As doped $\text{Ge}_{1-x}\text{As}_x\text{Te}$. The highest concentration of As resulted high resistivity and Seebeck coefficient.

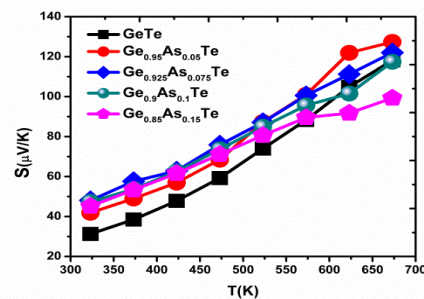


Fig. 4. The temperature dependent Seebeck coefficient of GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) samples.

Figure 5 describes the temperature dependence of power factor ($S^2\sigma$) of GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) samples. Characteristically GeTe having a very high electrical conductivity makes its $S^2\sigma$ value of $5 \mu\text{Wcm}^{-1}\text{K}^{-2}$ at 323 K rises to $23.91 \mu\text{Wcm}^{-1}\text{K}^{-2}$ at 673K, whereas $\text{Ge}_{0.9}\text{As}_{0.1}\text{Te}$ sample exhibits the $S^2\sigma$ value of $8 \mu\text{Wcm}^{-1}\text{K}^{-2}$ at 323 K and reaches the maximum value of $23 \mu\text{Wcm}^{-1}\text{K}^{-2}$ at 675 K. The scattering effects created by the secondary phase and atomic substitutions will effectively filter the charge carriers; which consequences the higher Seebeck coefficient to commitment the recovery loss in electrical conductivity of the system.¹⁶ An decrease in the population of carriers in the multiple flat valence bands at high temperature produces higher m^* ; which in turn results in an increase in S value before and after phase transition temperature, as S is directly related to m^* .^{17,18} These scattering effects which enhanced the Seebeck may also contribute for the reduction of the thermal conductivity.

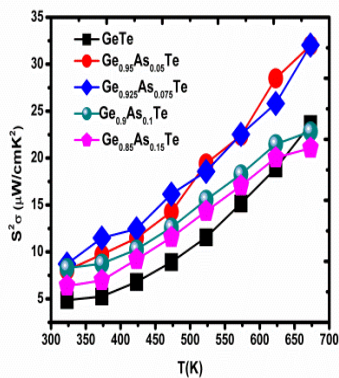


Fig. 5. The temperature dependent Seebeck coefficient of GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) samples.

Temperature dependent (300 – 673 K) thermal conductivity (κ) of these samples was shown in figure 6, which is calculated by the formula $\kappa = \frac{\rho}{\rho}$. Substitution about 10% of As in GeTe substantially reduces κ value. GeTe having the highest value of $\kappa \sim 6.5 \text{ Wm}^{-1}\text{K}^{-1}$ at 323 K; whereas $\text{Ge}_{0.9}\text{As}_{0.1}\text{Te}$ shows the lowest κ value of $4.37 \text{ Wm}^{-1}\text{K}^{-1}$, which is five times lower than that of pristine GeTe at 323K. A tremendous diminishing of κ values in 10 % of As doped sample is a consequence of low electronic contribution and preferential scattering.

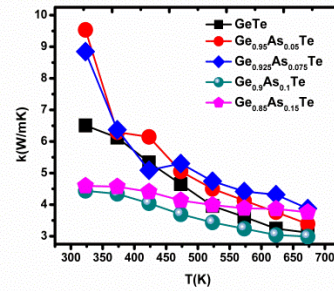


Fig. 6 The temperature dependent total thermal conductivity of GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) samples.

Figure 7 illustrates the temperature dependent figure of merit (ZT) of the GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) samples. Approximate power factor and low thermal conductivity of the $\text{Ge}_{0.9}\text{As}_{0.1}\text{Te}$ leads to the highest ZT of ~ 0.7 at 673K which is $\sim 10\%$ increment in GeTe. Therefore, the optimum doping level is achieved at 10 % As content in GeTe.

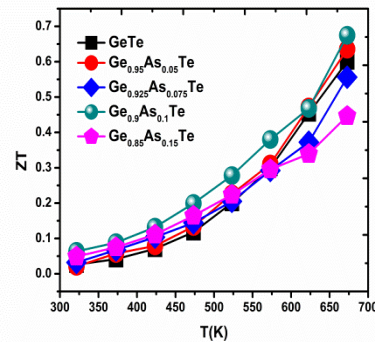


Fig. 7 The temperature dependent figure of merit (ZT) for GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) samples.

4. CONCLUSION

In the present investigation, we report systematic doping effects of As in GeTe on Thermoelectric properties. We successfully synthesized high-quality samples of GeTe and $\text{Ge}_{1-x}\text{As}_x\text{Te}$ ($x=0.05, 0.075, 0.1$ & 0.15) samples by solid state reaction and hot-press method. PXRD studies reveals that the samples are having rhombohedral structure at RT. These synthesized materials exhibit crystallographic phase changes at elevated temperatures, which is confirmed by synchrotron

XRD. From the results, As doping enhances the Seebeck coefficient in the temperature range of 323 to 673 K. The preferential scatterings by As secondary phase and point defect scattering have drastically reduced the thermal conductivity in $\text{Ge}_{0.9}\text{As}_{0.1}\text{Te}$ sample. In conclusion thermoelectric figure-of-merit (ZT) of GeTe is found to be as high as 0.7 at 673K for $\text{Ge}_{0.9}\text{As}_{0.1}\text{Te}$. The present results explore the synthesis and fundamental understanding of the structure-property relationship; we believe that this study on GeTe samples suitable for future design of the material for thermoelectric applications with ultimate figure-of-merit (ZT).

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References:

1. Yanagi, K. *et al.* Tuning of the Thermoelectric Properties of One-Dimensional Material Networks by Electric Double Layer Techniques Using Ionic Liquids. (2014). doi:10.1021/nl502982f
2. Cao, Q., Zheng, J., Zhang, K. & Ma, G. Thermoelectric properties of YbCd_2Sb_2 doped by Mg. **680**, 278–282 (2016).
3. Chen, Z., Zhou, B., Li, J. & Wen, C. Applied Surface Science Thermoelectric properties of Al-doped Mg_2Si thin films deposited by magnetron sputtering. *Appl. Surf. Sci.* **386**, 389–392 (2016).
4. Gayner, C. & Kar, K. K. Progress in Materials Science Recent advances in thermoelectric materials. *Prog. Mater. Sci.* **83**, 330–382 (2016).
5. Wang, H., Su, W., Liu, J. & Wang, C. Recent development of n-type perovskite thermoelectrics. *J. Mater.* (2016). doi:10.1016/j.jmat.2016.06.005
6. Li, J. *et al.* Electronic origin of the high thermoelectric performance of GeTe among the p-type group IV monotellurides. **9**, e353-8 (2017).
7. Li, L. & Snyder, G. J. Optimization of thermoelectric efficiency in SnTe : the case for the light band \dagger . *Phys. Chem. Chem. Phys.* **16**, 20741–20748 (2014).
8. Chattopadhyay, T. & Boucherle, J. Neutron diffraction study on the structural phase transition in GeTe. *J. Phys. C Solid State Phys.* **20**, 1431–1440 (1987).
9. Perumal, S., Roychowdhury, S., Negi, D. S., Datta, R. & Biswas, K. High Thermoelectric Performance and Enhanced Mechanical Stability of p-type $\text{Ge}_{1-x}\text{Sb}_x\text{Te}$. *Chem. Mater.* **27**, 7171–7178 (2015).
10. Kumar, A. *et al.* Phase Transitions of Thermoelectric TAGS-85. (2017). doi:10.1021/acs.inorgchem.7b02433
11. Liu, Z. *et al.* Phase-transition temperature suppression to achieve cubic GeTe and high thermoelectric performance by Bi and Mn codoping. (2018). doi:10.1073/pnas.1802020115
12. Siegrist, T. *et al.* Disorder-induced localization in crystalline phase-change materials. *Nat. Mater.* **10**, 202–208 (2011).
13. Williams, J. B. & Morelli, D. T. Understanding the superior thermoelectric performance of Sb precipitated $\text{Ge}_{17}\text{Sb}_2\text{Te}_{20}$. *J. Mater. Chem. C* **4**, 10011–10017 (2016).
14. Williams, J. B., Lara-Curzio, E., Cakmak, E., Watkins, T. & Morelli, D. T. Enhanced thermoelectric performance driven by high-temperature phase transition in the phase change material Ge_4SbTe_5 . *J. Mater. Res.* **30**, 2605–2610 (2015).
15. Rosenthal, T. *et al.* Enhancing the Thermoelectric Properties of Germanium Antimony Tellurides by Substitution with Selenium in Compounds. **2**, (2014).
16. Heremans, J. P., Thrush, C. M. & Morelli, D. T. Thermopower enhancement in PbTe with Pb precipitates. *J. Appl. Phys.* **98**, 0–6 (2005).
17. Snyder, G. J. & Toberer, E. S. Complex thermoelectric materials. **7**, 105–114 (2008).
18. Sootsman, J. R., Chung, D. Y. & Kanatzidis, M. G. New and old concepts in thermoelectric materials. *Angew. Chemie - Int. Ed.* **48**, 8616–8639 (2009).